

# A theoretical investigation on the $\text{Ti}(\text{H}_2\text{O})_n^{0,1+}$ ( $n = 1-5$ ) clusters by density functional theory methods

Ju-Guang Han, J.A. Morales \*

*Department of Chemistry and Biochemistry, Texas Tech University, P.O. Box 41061, Lubbock, TX 79409-1061, USA*

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## Abstract

The first systematic study of the  $\text{Ti}(\text{H}_2\text{O})_n^{0,1+}$  ( $n = 1-5$ ) series of clusters is herein presented at the level of the DFT B3LYP method in conjunction with electron core potential basis sets. The investigated structures are relevant for laser-induced and laser-ablation syntheses of titanium compounds, and also for fundamental spectroscopy studies of metal-bearing species in the gas phase. Calculated properties include optimal geometries, total energies, bond lengths, bond angles, natural orbital population analysis charges, and hydration dissociation energies inter alia. Present results reveal a strict correlation between the clusters total energy and their spin state. Without exception, the most stable neutral (cation) clusters  $\text{Ti}(\text{H}_2\text{O})_{1-5}^{0+}$  [ $\text{Ti}(\text{H}_2\text{O})_{1-5}^{1+}$ ] are those with spin state  $S = 1$  ( $S = 3/2$ ). Comparisons with a few available theoretical results show good agreement.

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## 1. Introduction

In recent years, there has been a renovated interest in studying ion–water clusters in the gas phase by both modern spectroscopic techniques and accurate computational methods [1]. From a practical point of view, this concern stems from the role played by ion–water clusters in atmospheric condensation, ion-induced nucleation and solvation. In fact, the ubiquity of dissolution and solvation processes in chemistry suffices to justify the relevance of contemporary ion–water clusters studies. At a more fundamental level, clusters can be viewed as a bridge between an isolated ion or molecule and the condensed phases. Consequently, the study of gas-phase clusters having one metal ion or atom coordinated with a few water molecules can elucidate many details of water–metal interactions. For example, the investigation of small water–metal clusters with the central metal in one of its stable oxidation states [e.g., Ti(IV) in  $\text{Ti}(\text{H}_2\text{O})_n^{4+}$  ( $n = 1-6$ ) or its hydrolyzed

forms:  $\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_n^{2+}$  ( $n = 1-4$ )] can be used as probes for the ion successive solvation processes in a size-dependent way over a relatively narrow range of cluster sizes. This is so because of the relatively short extension of the Debye length, i.e., the minimum separation over which neighboring ions in solution screen from each other. On the other hand, the study of small water–metal (or non-metal–metal [2]) clusters with the central atom at a very low or zero oxidation state [e.g., Ti(I) and Ti(0) in  $\text{Ti}(\text{H}_2\text{O})_n^{1+}$  and  $\text{Ti}(\text{H}_2\text{O})_n^{0+}$  ( $n = 1-5$ ), respectively] is highly relevant for laser-induced and laser-ablation syntheses of titanium compounds, and for fundamental spectroscopy studies of metal-bearing species in the gas phase.

A considerable number of both experimental and theoretical studies of aqueous clusters are known in the literature. Many of those recent investigations have focused on aqueous clusters bearing cations, (oxo) anions or small molecules of representative elements. For instance, Lisy and collaborators have exhaustively studied solvation effects in several clusters containing alkali metal ions coordinated with both water and non-aqueous solvents. These investigators have synthesized and characterized the first

\* Corresponding author. Tel.: +1 806 742 3094; fax: +1 806 742 1289.  
E-mail address: [jorge.morales@ttu.edu](mailto:jorge.morales@ttu.edu) (J.A. Morales).

genuine hexa-coordinated  $\text{Na}^{1+}$  ion cluster in the gas phase [3], prepared and measured the infrared spectra of the  $\text{Cs}^{1+}(\text{H}_2\text{O})_{1-5}$  series of clusters [4], inferred ion selectivity mechanisms in channel proteins by preparing and studying cluster prototypes of the form  $\text{M}^{1+}(\text{C}_6\text{H}_6)_n(\text{H}_2\text{O})_m$  with  $\text{M} = \text{Na}$  and  $\text{K}$  [5,6], and studied theoretically metallic ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ag}^+$ ), non-metallic ( $\text{NH}_4^+$ ), and organic [ $\text{C}(\text{NH}_2)_3^+$  and  $\text{N}(\text{CH}_3)_4^+$ ] cations solvated with different classes of  $\pi$  systems (e.g., ethene, benzene and pyrrole) [7]. Duncan and collaborators have investigated experimentally aqueous clusters containing alkaline-earth metal ions in their pioneering studies of the  $\text{Ca}^{1+}(\text{H}_2\text{O})$  [8] and  $\text{Mg}^{1+}(\text{H}_2\text{O})$  [9] complexes via photodissociation spectroscopy. Johnson and collaborators have also conducted extensive research on numerous aqueous clusters containing anions and small molecules, with special attention to solvation and dissociation mechanisms. Quite remarkably, these investigators could determine experimentally that the first primary hydration shells of the  $\text{OH}^-(\text{H}_2\text{O})_n$  and  $\text{F}^-(\text{H}_2\text{O})_n$  clusters in the gas phase do consist of exactly three and four  $\text{H}_2\text{O}$  molecules ( $n = 3$  and  $4$ ), respectively. Other important contributions by this group include their spectroscopic and theoretical studies of the  $\text{NO}^-(\text{H}_2\text{O})_{n=1-3}$  [10,11],  $\text{OH}^-(\text{H}_2\text{O})$  [12],  $(\text{H}_2\text{O})_6$  and  $(\text{H}_2\text{O})_6^-$  (“magic”) [13,14],  $\text{SO}_2^-(\text{H}_2\text{O})$  [15], and  $\text{X}^-(\text{H}_2\text{O})_2$ , ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) clusters [16,17] inter alia. The mentioned experiments have spurred a plethora of theoretical research on gas-phase aqueous clusters. Among several recent theoretical contributions, it is worth mentioning the quite successful application of the effective fragment potential (EFP) model by Gordon et al. [18] to study aqueous clusters as shown by the investigations on oxyanion–water clusters  $\text{A}^-(\text{H}_2\text{O})_{1-4}$  ( $\text{A}^- = \text{ClO}_4^-, \text{HSO}_4^-, \text{NO}_3^-, \text{H}_2\text{PO}_4^-, \text{HCO}_3^-, \text{HCO}_2^-, \text{SO}_4^{2-}, \text{HPO}_4^{2-}, \text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$ ) [19], alkali and alkaline-earth metal cation water clusters  $\text{M}(\text{H}_2\text{O})_{1-6}$  ( $\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) [20], and anion–water clusters  $\text{A}^-(\text{H}_2\text{O})_{1-6}$  ( $\text{A} = \text{OH}, \text{F}, \text{SH}, \text{Cl}$  and  $\text{Br}$ ) [21] by Merril et al., and by the study on  $\text{LiOH}$  dissociation in the  $\text{LiOH}(\text{H}_2\text{O})_n$ ,  $n = 1-6, 8$  clusters by Yoshikawa and Morales [22].

More recently, substantial efforts have been devoted to investigate different types of aqueous clusters containing transition metals as a way to elucidate chemical processes in both catalytic and biochemical systems [23]. Several experimental and theoretical studies of those types of clusters do exist in the literature but most of them deal with species having metals from the right half of the first transition row:  $\text{Mn}-\text{Cu}$  (e.g., studies of the iron-bearing aqueous clusters:  $\text{Fe}^{1+}(\text{H}_2\text{O})_{1-4}$  [24],  $\text{Fe}^{2+}(\text{H}_2\text{O})$  [25], and  $\text{Fe}^{1+}(\text{H}_2\text{O})$  [26] inter alia). In contrast, studies of aqueous clusters with metals from the left half of the first transition row:  $\text{Sc}-\text{Cr}$  are somewhat less common, especially in the case of scandium and titanium. Notable exceptions to that trend are the experimental investigations on the  $\text{V}(\text{H}_2\text{O})^{1+}$  complex by Brucat et al. [27], and on the  $\text{M}^{1+}(\text{H}_2\text{O})_{1-4}$ ,  $\text{M} = \text{Ti}-\text{Cu}$ , series of clusters by the Armentrout group [28].

Metallic titanium and its compounds have a broad range of application in chemistry. For instance, the aqueous chemistry of  $\text{Ti}(\text{IV})$ , the metal’s most stable form in solution, and also of  $\text{Ti}(\text{III})$ , a somewhat unstable form used as a strong reducer in analytical chemistry [29], are routine topics in chemistry textbooks [29]. Pure titanium enters in the composition of special types of steel; titanium dioxide,  $\text{TiO}_2$ , is a white pigment with widespread applications in paints, ceramics, cosmetics, and paper manufacturing; and some “*titanates*” exhibit ferroelectric properties [29]. More importantly, titanium organo-compounds have a great deal of applications as catalysts and intermediaries in the synthesis of several organic compounds, as is the case of the celebrated Ziegler–Natta procedure to manufacture polyethylene and polypropylene [29,30]. In view of those applications, a number of fundamental studies of small titanium-bearing compounds exist in the literature. Some examples from the experimental field are the gas-phase synthesis of the  $\text{TiO}(\text{H}_2\text{O})_n^{1+}$  clusters ions by laser-induced  $\text{Ti}-\text{H}_2\text{O}$  plasma reactions by Deng et al. [31], the formation and further study of the  $\text{HM}(\text{OH})$  and  $\text{H}_2\text{M}(\text{OH})_2$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ) molecules from laser-ablated metal atoms by Zhou et al. [32], and the aforesaid study of the  $\text{M}^{1+}(\text{H}_2\text{O})_{1-4}$ ,  $\text{M} = \text{Ti}-\text{Cu}$ , series of clusters by the Armentrout group [28]. Relevant theoretical studies of small titanium-bearing compounds are the self-consistent field (SCF) Hartree–Fock (HF) investigation on ligand-field effects in hexa-aquo divalent (II) and trivalent (III) transition metal ions including titanium by Akesson et al. [33], the density functional theory (DFT) calculations of the  $\text{M}^{3+}(\text{H}_2\text{O})_6$ ,  $\text{M} = \text{Sc}-\text{Fe}$ , series of ions by Kallies and Meier [34], the theoretical determination of hydration binding energies in the  $\text{M}^{1,2+}(\text{H}_2\text{O})_{1-2}$ ,  $\text{M} = \text{Sc}-\text{Zn}$ , ions at the self-consistent field modified coupled pair functional (SCF-MCPF) level by Rosi and Bauschlicher [35], and the DFT studies of water exchange reactions and hydrolysis in the  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  ions by Hartmann et al. [36]. Quite remarkably, one of the most interesting theoretical studies of titanium compounds is the ab initio investigation on the isomerizations of  $\text{Ti}(\text{H}_2\text{O})$  and on the unimolecular decomposition mechanisms of  $\text{Ti}-\text{H}_3\text{OH}$  at the complete active space self-consistent field (CASSCF) level by Kudo and Gordon [37]. Their complete study also includes the characterization of several geometries at the ground and lowest excited states and the determination of their potential energy surfaces for diverse unimolecular decomposition reactions [37].

Despite all the previous efforts, the theoretical understanding of the whole series of aqueous titanium clusters:  $\text{Ti}(\text{H}_2\text{O})_{1-6}^{0,4+}$  in the gas phase still remains fragmentary. Therefore, we present herein the first complete theoretical characterization of the series of the lowest-charged aqueous titanium clusters:  $\text{Ti}(\text{H}_2\text{O})_n^{0,1+}$  ( $n = 1-5$ ) in the gas phase. These types of titanium-bearing compounds are relevant for laser-induced and laser-ablation syntheses of titanium compounds [31,32]; and for fundamental spectroscopy studies of metal-bearing species in the gas phase, as those previously conducted by the Duncan [8,9], Brucat [27], and Armentrout [28] groups. Therefore,

this article intends to provide the first theoretical description of the geometries, molecular properties, and relative stabilities of the whole series of the  $\text{Ti}(\text{H}_2\text{O})_n^{0,1+}$  ( $n = 1-5$ ) clusters as a guide for future experimental studies of these fascinating structures.

## 2. Computational details

The explicit treatment of all the electrons in this type of clusters constitutes a demanding computational task. One of the best ways to surmount this difficulty is to make use of electron core potentials (ECP), also known as pseudo-potentials [38], by means of which only the valence electrons are treated explicitly. Therefore, the complete series of the  $\text{Ti}(\text{H}_2\text{O})_n^{0,1+}$  ( $n = 1-5$ ) clusters are herein calculated at the DFT level of theory with the unrestricted (U), hybrid Becke (B3) [39] exchange and the Lee, Yang and Parr (LYP) [40] correlation functionals [DFT-(U)B3LYP] in conjunction with the Los Alamos ECP double-zeta basis sets (LanL2DZ) [41,42] for the Ti atom and with the ordinary, non-ECP, all-electron 6-31+G\* basis set for the H and O atoms [DFT-(U)B3LYP/LanL2DZ/6-31+G\*]. The combination of an ECP basis set with DFT exchange-correlation functionals might give rise to some reservations because those functionals were originally formulated for core-and-valence electrons basis sets and not for a combination of an ECP with valence electrons. However, the validity and accuracy of the proposed methodology have been established in previous theoretical investigations on similar systems [43–45] and finally summarized in [2].

All the present DFT-(U)B3LYP/LanL2DZ/6-31+G\* computations are performed with the Gaussian 98 program [46]. Each cluster in the  $\text{Ti}(\text{H}_2\text{O})_n^{0,1+}$  ( $n = 1-5$ ) series is first geometry optimized at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level for different spin states  $S$  and the converged structures are subsequently tested for stability by harmonic vibrational frequency analysis. The unrestricted Kohn–Sham (KS) single determinant implicit in the present method is not a spin eigenfunction in general and therefore the obtained states might be spin-contaminated. However, the degree of spin contamination in all the presently calculated species turns out to be relatively low. For instance, in the attempted singlet ( $S = 0$ ), triplet ( $S = 1$ ), and quintet ( $S = 2$ ) states of the trial molecule TiO (see below), the KS single determinant expectation values of the total spin operator  $\hat{S}^2$  are successively:  $\langle \hat{S}^2 \rangle = 0.000 = S(S + 1) = 0(0 + 1) = 0$ ,  $\langle \hat{S}^2 \rangle = 2.051 \approx S(S + 1) = 1(1 + 1) = 2$ , and  $\langle \hat{S}^2 \rangle = 6.004 \approx S(S + 1) = 2(2 + 1) = 6$ ; whereas, in the attempted singlet ( $S = 0$ ) and quartet ( $S = 3/2$ ) states of the  $\text{Ti}(\text{H}_2\text{O})_1^{0+}$  and  $\text{Ti}(\text{H}_2\text{O})_{12}^{1+}$  clusters, the expectation value of  $\hat{S}^2$  are, respectively:  $\langle \hat{S}^2 \rangle = 0.000 = S(S + 1) = 0(0 + 1)$  and  $\langle \hat{S}^2 \rangle = 3.752 \approx S(S + 1) = 3/2(3/2 + 1) = 3.75$ . The present geometry optimization procedure imposes no constraints on bonds and angles and starts with geometry guesses of relatively high symmetry. For instance, in the case of the  $\text{Ti}(\text{H}_2\text{O})_4^{0,1+}$  clusters, different types of approximately planar, seesaw, and tetrahedral arrangements of

the  $\text{H}_2\text{O}$  molecules around the  $\text{Ti}^{0,1+}$  atom/ion are employed as initial guesses; whereas, in the case of the  $\text{Ti}(\text{H}_2\text{O})_5^{0,1+}$  clusters, different types of approximately planar, trigonal bipyramidal, and square pyramidal arrangements are used. If a converged cluster is found to be unstable, efforts are made to obtain a stable structure by deforming its geometry along its unstable coordinates. In most cases, some degree of symmetry is lost during that deformation procedure. The lengthy details of the geometry optimizations through coordinate relaxation are omitted for shortness and only the finally stable structures are reported below. In general, obtaining converged and stable structures for this type of clusters has proven to be difficult, especially in the cases of the neutral species. After a stable structure is found, its different molecular properties, including bond lengths and angles, total energies, and natural orbital population analysis charges, are subsequently calculated. In addition, two important properties to ascertain the stability of the studied structures are their successive hydration dissociation energies  $DE_C(n, n - 1)$  and  $DE_N(n, n - 1)$  for the charged and neutral clusters, respectively, defined according to

$$DE_C(n, n - 1) = E(\text{H}_2\text{O}) + E_T[\text{Ti}(\text{H}_2\text{O})_{n-1}^{1+}] - E_T[\text{Ti}(\text{H}_2\text{O})_n^{1+}],$$

$$DE_N(n, n - 1) = E(\text{H}_2\text{O}) + E_T[\text{Ti}(\text{H}_2\text{O})_{n-1}^{0+}] - E_T[\text{Ti}(\text{H}_2\text{O})_n^{0+}]$$

where  $E(\text{H}_2\text{O})$  is the energy of an isolated  $\text{H}_2\text{O}$  molecule at the B3LYP/6-31+G\* level ( $-76.4212204$  hartree), and  $E_T[\text{Ti}(\text{H}_2\text{O})_n^{0,1+}]/E_T[\text{Ti}(\text{H}_2\text{O})_{n-1}^{0,1+}]$  are the total energies of the calculated  $\text{Ti}(\text{H}_2\text{O})_n^{0,1+}/\text{Ti}(\text{H}_2\text{O})_{n-1}^{0,1+}$  clusters at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level. Some relevant values of  $DE_C(n, n - 1)$  and  $DE_N(n, n - 1)$  are presented and discussed below.

## 3. Results and discussions

The most relevant calculated properties of the  $\text{Ti}(\text{H}_2\text{O})_n^{0,1+}$  ( $n = 1-5$ ) series of clusters at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level are listed in Tables 1–6. The clusters total energies  $E_T$  along with their representative bond lengths  $R_1-R_5$  and bond angles  $a_1-a_5$  are presented in Tables 1–5; additionally, the clusters natural orbital population analysis charges and electron configurations on the Ti and O atoms are listed in Table 6. The structures of the most representative  $\text{Ti}(\text{H}_2\text{O})_n^{0,1+}$  ( $n = 1-5$ ) clusters per each number  $n$  of coordinated  $\text{H}_2\text{O}$  molecules along with their bond lengths  $R_1-R_5$  and bond angles  $a_1-a_5$  are depicted in Fig. 1. Additional calculated properties, such as hydration dissociation energies, are presented and discussed below.

In order to preliminarily assess the accuracy of the proposed method in the description of titanium-bearing compounds, the simple TiO molecule is first optimized at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level; the predicted Ti–O bond length of 1.652 Å in TiO agrees well with the experimental data [32].

Table 1  
Geometries and total energies of  $\text{Ti}(\text{H}_2\text{O})^{0,+1}$  clusters at the DFT-(U)B3LYP /LanL2DZ/6-31+G\* level

System	Sym.	Spin	$R_1$	$R_2$	$a_1$	$a_2$	$E_T$
$\text{Ti}(\text{H}_2\text{O})^0$	$C_s$	0	2.062	0.990	104.6	106.8	-134.3663726
		1	2.123	0.980	116.8	108.1	-134.4173816
		2	2.338	0.974	116.8	106.3	-134.4058719
$\text{Ti}(\text{H}_2\text{O})^{1+}$	$C_s$	1/2	2.098	0.976	126.5	107.0	-134.1963648
		3/2	2.109	0.975	126.6	106.9	-134.2194973

Units: bond lengths  $R_1$ – $R_2$ , Å; bond angles  $a_1$ – $a_2$ , °; total energy  $E_T$ , hartree.

Table 2  
Geometries and total energies of  $\text{Ti}(\text{H}_2\text{O})_2^{0,\pm 1}$  clusters at the DFT-(U)B3LYP /LanL2DZ/6-31+G\* level

System	Sym.	Spin	$R_1$	$R_2$	$R_3$	$R_4$	$a_1$	$a_2$	$a_3$	$E_T$
$\text{Ti}(\text{H}_2\text{O})_2^0$	$C_1$	0	2.139	2.139	0.983	0.983	111.6	107.6	177.4	-210.8576164
		1	2.152	2.152	0.982	0.983	111.4	108.4	176.3	-210.873982
		2	2.232	2.229	0.979	0.978	122.2	126.7	157.0	-210.8421159
$\text{Ti}(\text{H}_2\text{O})_2^{1+}$	$D_{2d}$	1/2	2.128	2.128	0.975	0.975	126.1	126.1	90.0	-210.6471726
		3/2	2.136	2.136	0.975	0.975	126.2	126.2	90.0	-210.6886059
$\text{Ti}(\text{H}_2\text{O})_2^{-1}$	$C_1$	1/2	2.137	2.137	0.995	0.994	110.0	111.6	166.8	-210.8773796

Units: bond lengths  $R_1$ – $R_4$ , Å; bond angles  $a_1$ – $a_3$ , °; total energy  $E_T$ , hartree.

Table 3  
Geometries and total energies of  $\text{Ti}(\text{H}_2\text{O})_3^{0,1+}$  clusters at the DFT-(U)B3LYP /LanL2DZ/6-31+G\* level

System	Sym.	Spin	$R_1$	$R_2$	$R_3$	$a_1$	$a_2$	$a_3$	$E_T$
$\text{Ti}(\text{H}_2\text{O})_3^0$	$C_1$	0	2.120	2.178	2.345	165.2	70.7	123.9	-287.2936164
		1	2.141	2.161	2.153	143.9	91.9	123.8	-287.3071683
		2	2.132	2.152	2.152	133.9	89.4	136.7	-287.2796723
$\text{Ti}(\text{H}_2\text{O})_3^{1+}$	$C_1$	1/2	2.134	2.133	2.138	121.1	115.7	121.3	-287.1434916
		3/2	2.147	2.151	2.146	120.7	116.4	120.9	-287.1578887

Units: bond lengths  $R_1$ – $R_3$ , Å; bond angles  $a_1$ – $a_3$ , °; total energy  $E_T$ , hartree.

Table 4  
Geometries and total energies of  $\text{Ti}(\text{H}_2\text{O})_4^{0,1+}$  clusters at the DFT-(U)B3LYP /LanL2DZ/6-31+G\* level

System	Sym.	Spin	$R_1$	$R_2$	$R_3$	$R_4$	$a_1$	$a_2$	$a_3$	$a_4$	$E_T$
$\text{Ti}(\text{H}_2\text{O})_4^0$	$C_1$	0	2.268	2.116	2.116	2.180	105.0	78.2	80.0	106.6	-363.7032244
		1	2.172	2.179	2.200	2.242	95.9	97.3	79.6	87.9	-363.7520216
		2	2.187	2.187	2.186	2.187	93.2	86.7	93.3	86.7	-363.7283313
$\text{Ti}(\text{H}_2\text{O})_4^{1+}$	$C_1$	1/2	2.227	2.157	2.227	2.157	83.5	96.4	83.5	96.4	-363.599257
		3/2	2.211	2.188	2.214	2.187	88.2	89.9	90.3	91.6	-363.6112677

Units: bond lengths  $R_1$ – $R_4$ , Å; bond angles  $a_1$ – $a_4$ , °; total energy  $E_T$ , hartree.

Table 5  
Geometries and total energies of  $\text{Ti}(\text{H}_2\text{O})_5^{0,1+}$  clusters at the DFT-(U)B3LYP /LanL2DZ/6-31+G\* level

System	Sym.	Spin	$R_1$	$R_2$	$R_3$	$R_4$	$R_5$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$E_T$
$\text{Ti}(\text{H}_2\text{O})_5^0$	$C_1$	0	2.163	2.163	2.161	2.170	2.159	95.6	83.1	98.7	83.2	84.9	-440.138935
		1	2.226	2.231	2.252	2.250	2.340	100.7	76.2	107.8	107.8	74.2	-440.1893493
		2	2.301	2.207	2.206	2.303	2.223	80.4	93.3	80.3	106.0	83.8	-440.1704495
$\text{Ti}(\text{H}_2\text{O})_5^{1+}$	$C_1$	1/2	2.174	2.192	2.194	2.208	2.311	87.4	91.1	95.1	86.3	101.4	-440.0416531
		3/2	2.317	2.290	2.193	2.292	2.312	74.5	77.1	97.1	113.8	71.9	-440.0544594

Units: bond lengths  $R_1$ – $R_5$ , Å; bond angles  $a_1$ – $a_5$ , °; total energy  $E_T$ , hartree.

Table 6  
Natural orbital population analysis charges and natural orbital electron configurations of the Ti and O atoms in the  $\text{Ti}(\text{H}_2\text{O})_n^{0,1+}$  ( $n = 1-5$ ) clusters

System	Sym.	Spin	Atom	Natural pop. charge	Natural electron configuration	
$\text{Ti}(\text{H}_2\text{O})^0$	$C_s$	0	Ti	-0.0357	[core]4s <sup>1.62</sup> 3d <sup>2.41</sup>	
			O	-1.0185	[core]2s <sup>1.77</sup> 2p <sup>5.23</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
		1	Ti	-0.0242	[core]4s <sup>1.70</sup> 3d <sup>2.31</sup>	
			O	-1.0398	[core]2s <sup>1.76</sup> 2p <sup>5.25</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
		2	Ti	0.0065	[core]4s <sup>0.96</sup> 3d <sup>3.02</sup> 4p <sup>0.01</sup>	
O	-1.0362	[core]2s <sup>1.76</sup> 2p <sup>5.24</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>				
$\text{Ti}(\text{H}_2\text{O})^{1+}$	$C_s$	1/2	Ti	0.9328	[core]4s <sup>0.59</sup> 3d <sup>2.47</sup>	
			O	-1.0550	[core]2s <sup>1.75</sup> 2p <sup>5.31</sup> 3p <sup>0.01</sup>	
		3/2	Ti	0.9374	[core]4s <sup>0.47</sup> 3d <sup>2.59</sup>	
			O	-1.0573	[core]2s <sup>1.75</sup> 2p <sup>5.30</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
$\text{Ti}(\text{H}_2\text{O})_2^0$	$C_1$	0	Ti	-0.0466	[core]4s <sup>1.56</sup> 3d <sup>2.46</sup> 4p <sup>0.01</sup> 4d <sup>0.01</sup>	
			O(1)	-1.0174	[core]2s <sup>1.76</sup> 2p <sup>5.24</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			O(2)	-1.0174	[core]2s <sup>1.76</sup> 2p <sup>5.24</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			Ti	-0.0331	[core]4s <sup>1.58</sup> 3d <sup>2.43</sup> 4p <sup>0.01</sup> 4d <sup>0.01</sup>	
			O(1)	-1.0234	[core]2s <sup>1.76</sup> 2p <sup>5.24</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			O(2)	-1.0234	[core]2s <sup>1.76</sup> 2p <sup>5.24</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
		1	2	Ti	0.0582	[core]4s <sup>0.85</sup> 3d <sup>3.07</sup> 4p <sup>0.01</sup> 5s <sup>0.01</sup> 4d <sup>0.01</sup>
				O(1)	-1.0381	[core]2s <sup>1.75</sup> 2p <sup>5.26</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>
				O(2)	-1.0381	[core]2s <sup>1.75</sup> 2p <sup>5.26</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>
			3/2	Ti	0.8326	[core]4s <sup>0.53</sup> 3d <sup>2.64</sup> 4d <sup>0.01</sup>
				O(1,2)	-1.0426	[core]2s <sup>1.74</sup> 2p <sup>5.29</sup> 3d <sup>0.01</sup>
				Ti	0.8414	[core]4s <sup>0.51</sup> 3d <sup>2.65</sup> 4d <sup>0.01</sup>
O(1,2)	-1.0453	[core]2s <sup>1.74</sup> 2p <sup>5.29</sup> 3d <sup>0.01</sup>				
$\text{Ti}(\text{H}_2\text{O})_2^{1+}$	$D_{2d}$	1/2	Ti	-0.6328	[core]4s <sup>1.58</sup> 3d <sup>2.42</sup> 4p <sup>0.61</sup> 4d <sup>0.01</sup>	
			O(1)	-1.0890	[core]2s <sup>1.77</sup> 2p <sup>5.25</sup> 3s <sup>0.04</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>	
			O(2)	-1.0892	[core]2s <sup>1.77</sup> 2p <sup>5.25</sup> 3s <sup>0.04</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>	
$\text{Ti}(\text{H}_2\text{O})_3^0$	$C_1$	0	Ti	-0.0515	[core]4s <sup>1.48</sup> 3d <sup>2.54</sup> 4p <sup>0.01</sup> 4d <sup>0.02</sup>	
			O(1)	-1.0127	[core]2s <sup>1.76</sup> 2p <sup>5.23</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			O(2)	-1.0125	[core]2s <sup>1.74</sup> 2p <sup>5.24</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			O(3)	-1.0380	[core]2s <sup>1.76</sup> 2p <sup>5.24</sup> 3s <sup>0.01</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>	
			Ti	0.0175	[core]4s <sup>1.45</sup> 3d <sup>2.50</sup> 4p <sup>0.01</sup> 4d <sup>0.02</sup>	
			O(1)	-1.0184	[core]2s <sup>1.75</sup> 2p <sup>5.25</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
		1	2	O(2)	-1.0457	[core]2s <sup>1.76</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>
				O(3)	-1.0368	[core]2s <sup>1.76</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>
				Ti	0.3767	[core]4s <sup>0.63</sup> 3d <sup>2.61</sup> 4p <sup>0.36</sup> 5s <sup>0.01</sup> 4d <sup>0.02</sup>
			3/2	O(1)	-1.0744	[core]2s <sup>1.74</sup> 2p <sup>5.28</sup> 3s <sup>0.05</sup>
				O(2)	-1.0636	[core]2s <sup>1.76</sup> 2p <sup>5.25</sup> 3s <sup>0.02</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>
				O(3)	-1.0650	[core]2s <sup>1.76</sup> 2p <sup>5.25</sup> 3s <sup>0.03</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>
$\text{Ti}(\text{H}_2\text{O})_3^{1+}$	$C_1$	1/2	Ti	0.8038	[core]4s <sup>0.60</sup> 3d <sup>2.58</sup> 4d <sup>0.02</sup>	
			O(1)	-1.0255	[core]2s <sup>1.73</sup> 2p <sup>5.28</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			O(2)	-1.0251	[core]2s <sup>1.73</sup> 2p <sup>5.28</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			O(3)	-1.0256	[core]2s <sup>1.73</sup> 2p <sup>5.28</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			Ti	0.7988	[core]4s <sup>0.54</sup> 3d <sup>2.65</sup> 4d <sup>0.01</sup>	
			O(1,2)	-1.024	[core]2s <sup>1.73</sup> 2p <sup>5.28</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
		3/2	O(3)	-1.023	[core]2s <sup>1.73</sup> 2p <sup>5.27</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			0	Ti	0.1337	[core]4s <sup>1.11</sup> 3d <sup>2.68</sup> 4p <sup>0.05</sup> 5s <sup>0.01</sup> 4d <sup>0.02</sup>
				O(1)	-1.0123	[core]2s <sup>1.75</sup> 2p <sup>5.24</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>
O(2)	-1.0183	[core]2s <sup>1.75</sup> 2p <sup>5.22</sup> 3s <sup>0.01</sup> 3p <sup>0.03</sup> 3d <sup>0.01</sup>				
O(3)	-0.9911	[core]2s <sup>1.74</sup> 2p <sup>5.23</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>				
O(4)	-1.0238	[core]2s <sup>1.76</sup> 2p <sup>5.22</sup> 3p <sup>0.03</sup> 4s <sup>0.01</sup> 3d <sup>0.01</sup>				
1	Ti	-0.0329		[core]4s <sup>1.36</sup> 3d <sup>2.61</sup> 4p <sup>0.02</sup> 4d <sup>0.04</sup>		
	O(1)	-1.0339		[core]2s <sup>1.76</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>		
	O(2)	-1.0050		[core]2s <sup>1.75</sup> 2p <sup>5.24</sup> 3s <sup>0.01</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>		
	O(3)	-1.0258		[core]2s <sup>1.74</sup> 2p <sup>5.23</sup> 3s <sup>0.01</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>		
	O(4)	-1.0219	[core]2s <sup>1.76</sup> 2p <sup>5.24</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>			
	Ti	0.306	[core]4s <sup>0.57</sup> 3d <sup>2.62</sup> 4p <sup>0.47</sup> 5s <sup>0.01</sup> 4d <sup>0.03</sup>			
2	O(1,4)	-1.0275	[core]2s <sup>1.74</sup> 2p <sup>5.24</sup> 3s <sup>0.02</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>			
	O(2)	-1.0274	[core]2s <sup>1.74</sup> 2p <sup>5.24</sup> 3s <sup>0.02</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>			
	O(3)	-1.0276	[core]2s <sup>1.74</sup> 2p <sup>5.24</sup> 3s <sup>0.02</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>			

(continued on next page)

Table 6 (continued)

System	Sym.	Spin	Atom	Natural pop. charge	Natural electron configuration	
Ti(H <sub>2</sub> O) <sub>4</sub> <sup>1+</sup>	C <sub>1</sub>	1/2	Ti	0.7331	[core]4s <sup>0.61</sup> 3d <sup>2.63</sup> 5s <sup>0.01</sup> 4d <sup>0.03</sup>	
			O(1,3)	−0.9999	[core]2s <sup>1.73</sup> 2p <sup>5.26</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>	
			O(2,4)	−1.0195	[core]2s <sup>1.73</sup> 2p <sup>5.27</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>	
	3/2	Ti	0.7284	[core]4s <sup>0.52</sup> 3d <sup>2.72</sup> 5s <sup>0.01</sup> 4d <sup>0.03</sup>		
		O(1,3)	−1.0078	[core]2s <sup>1.73</sup> 2p <sup>5.26</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>		
		O(2,4)	−1.001	[core]2s <sup>1.73</sup> 2p <sup>5.26</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>		
Ti(H <sub>2</sub> O) <sub>5</sub> <sup>0</sup>	C <sub>1</sub>	0	Ti	−0.006	[core]4s <sup>1.32</sup> 3d <sup>2.60</sup> 4p <sup>0.04</sup> 4d <sup>0.04</sup>	
			O(1)	−1.016	[core]2s <sup>1.75</sup> 2p <sup>5.24</sup> 3s <sup>0.01</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			O(2)	−1.001	[core]2s <sup>1.74</sup> 2p <sup>5.24</sup> 3s <sup>0.01</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			O(3)	−1.013	[core]2s <sup>1.74</sup> 2p <sup>5.24</sup> 3s <sup>0.01</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			O(4)	−1.006	[core]2s <sup>1.75</sup> 2p <sup>5.24</sup> 3s <sup>0.01</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>	
			O(5)	−1.087	[core]2s <sup>1.77</sup> 2p <sup>5.25</sup> 3s <sup>0.02</sup> 3p <sup>0.04</sup> 3d <sup>0.01</sup>	
			1	Ti	0.0623	[core]4s <sup>1.24</sup> 3d <sup>2.56</sup> 4p <sup>0.09</sup> 4d <sup>0.05</sup>
				O(1)	−1.0322	[core]2s <sup>1.75</sup> 2p <sup>5.24</sup> 3s <sup>0.01</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>
				O(2)	−1.0186	[core]2s <sup>1.74</sup> 2p <sup>5.24</sup> 3s <sup>0.01</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>
	2	O(3)	−1.0372	[core]2s <sup>1.76</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>		
		O(4)	−1.0430	[core]2s <sup>1.76</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3p <sup>0.01</sup> 3d <sup>0.01</sup>		
		O(5)	−1.0586	[core]2s <sup>1.77</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3p <sup>0.02</sup> 3d <sup>0.01</sup>		
		Ti	0.2615	[core]4s <sup>0.64</sup> 3d <sup>2.64</sup> 4p <sup>0.37</sup> 5s <sup>0.03</sup> 4d <sup>0.05</sup>		
		O(1)	−1.012	[core]2s <sup>1.75</sup> 2p <sup>5.24</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>		
		O(2)	−1.037	[core]2s <sup>1.74</sup> 2p <sup>5.24</sup> 3s <sup>0.01</sup> 3p <sup>0.04</sup> 3d <sup>0.01</sup>		
	Ti(H <sub>2</sub> O) <sub>5</sub> <sup>1+</sup>	C <sub>1</sub>	1/2	Ti	0.7577	[core]4s <sup>0.66</sup> 3d <sup>2.50</sup> 4p <sup>0.01</sup> 5s <sup>0.01</sup> 4d <sup>0.06</sup>
				O(1)	−1.0054	[core]2s <sup>1.73</sup> 2p <sup>5.26</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>
				O(2)	−1.0186	[core]2s <sup>1.73</sup> 2p <sup>5.26</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>
O(3)				−1.0034	[core]2s <sup>1.73</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>	
O(4)				−1.0123	[core]2s <sup>1.73</sup> 2p <sup>5.26</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>	
O(5)				−1.0576	[core]2s <sup>1.75</sup> 2p <sup>5.26</sup> 3s <sup>0.01</sup> 3p <sup>0.03</sup> 3d <sup>0.01</sup>	
3/2				Ti	0.715	[core]4s <sup>0.47</sup> 3d <sup>2.77</sup> 5s <sup>0.01</sup> 4d <sup>0.04</sup>
				O(1)	−1.017	[core]2s <sup>1.74</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>
				O(2)	−1.009	[core]2s <sup>1.74</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>
3/2	O(3)	−1.000	[core]2s <sup>1.73</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>			
	O(4)	−1.012	[core]2s <sup>1.74</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>			
	O(5)	−1.007	[core]2s <sup>1.74</sup> 2p <sup>5.25</sup> 3s <sup>0.01</sup> 3d <sup>0.01</sup>			

### 3.1. Ti(H<sub>2</sub>O)<sub>0,1+</sub> clusters

Neutral Ti(H<sub>2</sub>O)<sub>0</sub> clusters with C<sub>2v</sub> and C<sub>s</sub> point-group symmetries and with spin states  $S=0, 1$  and  $2$  are optimized at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis reveals that only the converged C<sub>s</sub> structures are stable. Inspection of the theoretical results listed in Table 1 shows that in these Ti(H<sub>2</sub>O)<sub>0</sub> clusters the Ti–O bond length  $R_1$  monotonically and the bond angle  $a_1$  almost monotonically increase as the spin number  $S$  varies from  $0$  to  $2$ , whereas the total energy  $E_T$  reaches a minimum with  $S=1$ . Therefore, the Ti(H<sub>2</sub>O)<sub>0</sub> cluster with spin state  $S=1$  is the most stable structure in this series of Ti(H<sub>2</sub>O)<sub>0</sub> clusters. The electronic state in that structure is <sup>3</sup>A'. The Ti–O bond length  $R_1$  in the most stable Ti(H<sub>2</sub>O)<sub>0</sub> cluster with  $S=1$  at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level is of 2.123 Å, a value that is appreciably longer than the Ti–O bond lengths in both the TiO molecule at the same level of theory (1.652 Å) and in the Ti(H<sub>2</sub>O)<sub>0</sub> molecule at the CASSCF level [37], respectively. This suggests that the interaction between the Ti atom and the H<sub>2</sub>O molecule in Ti(H<sub>2</sub>O)<sub>0</sub> is

mainly through weak van der Waals forces as expected if the Ti and the H<sub>2</sub>O remain uncharged upon coordination. That charge neutrality is in fact corroborated by the natural orbital population analysis charges of the Ti(H<sub>2</sub>O)<sub>0</sub> clusters listed in Table 6. There, it is clearly shown that the charge on the Ti atom is always negligible in each cluster although slightly and monotonically increases with the spin number  $S$ . It is instructive to compare the present results of the Ti(H<sub>2</sub>O)<sub>0</sub> cluster with  $S=1$  with those of the related TiH<sub>3</sub>OH molecule at the CASSCF level [37]. The presently calculated Ti–O and O–H bond lengths  $R_1$  and  $R_2$  and the H–O–H bond angle  $a_2$  of the most stable Ti(H<sub>2</sub>O)<sub>0</sub> cluster with  $S=1$  are: 2.123 Å, 0.98 Å and 108.1°, respectively, values that compare well with their analogous ones of 2.180 Å, 0.97 Å and 108.2°, respectively, in the TiH<sub>3</sub>OH molecule at the CASSCF level [37].

Cation Ti(H<sub>2</sub>O)<sub>1+</sub> clusters with C<sub>s</sub> point-group symmetry and with spin states  $S=1/2$  and  $3/2$  are optimized at the (U)B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis reveals that all the converged structures are stable without exception. Inspection of the theoretical results listed in Table 1 reveals that

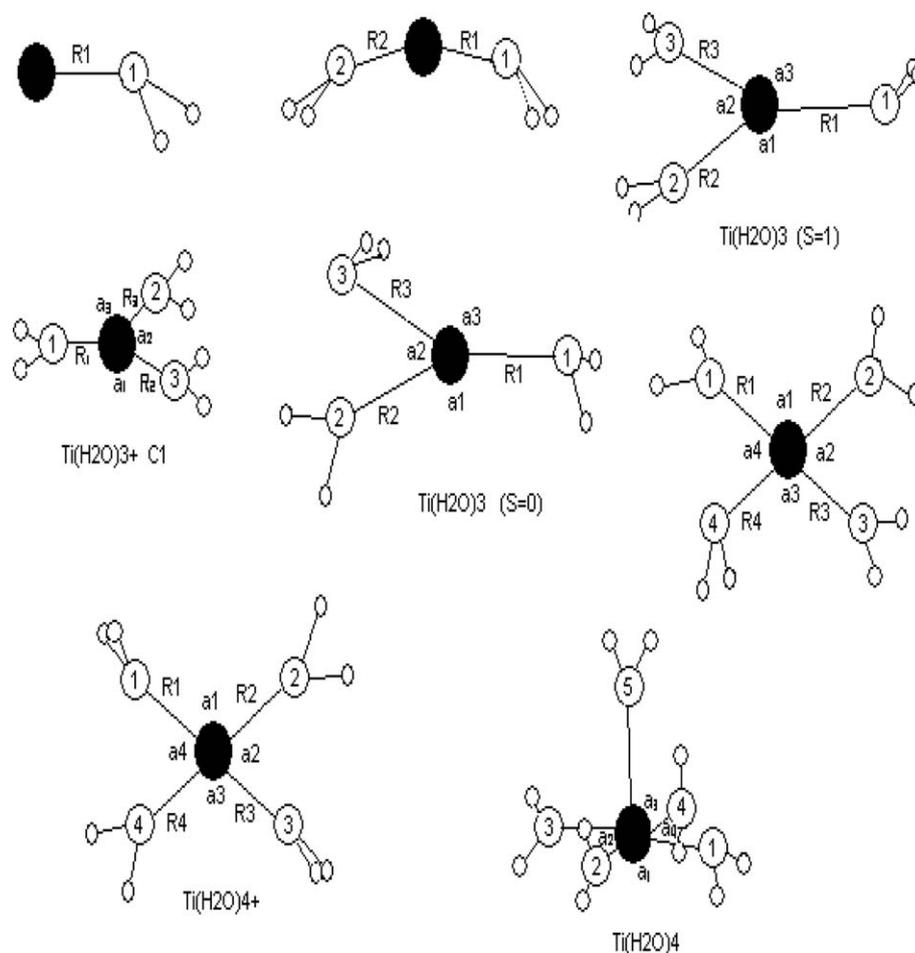


Fig. 1. Structures, bond lengths  $R_1$ – $R_4$ , and bond angles  $a_1$ – $a_4$ , of representative  $\text{Ti}(\text{H}_2\text{O})_n^{0,+}$  ( $n = 1$ – $5$ ) clusters at the DFT-(U)B3LYP/LanL2DZ/6-31+G\* level.

the Ti–O bond length  $R_1$  in the  $\text{Ti}(\text{H}_2\text{O})^{1+}$  clusters increases monotonically as the spin number  $S$  varies from  $1/2$  to  $3/2$ , whereas the total energy  $E_T$  reaches a minimum with  $S = 3/2$ . Therefore, the  $\text{Ti}(\text{H}_2\text{O})^{1+}$  cluster with spin state  $S = 3/2$  is the most stable structure in the series of  $\text{Ti}(\text{H}_2\text{O})^{1+}$  clusters. The electronic state in that structure is  $^4A'$ . Despite charged Ti atoms, the Ti–O bond lengths  $R_1$  in the  $\text{Ti}(\text{H}_2\text{O})^{1+}$  clusters with spin numbers  $S = 1/2$  and  $3/2$  slightly differ from those in their neutral counterparts with spin numbers  $S = 0$  and  $S = 1$ , respectively. However, the Ti–O bond length  $R_1$  of 2.109 Å in the most stable  $\text{Ti}(\text{H}_2\text{O})^{1+}$  cluster with  $S = 3/2$  at the (U)B3LYP/LanL2DZ/6-31+G\* level compares well with its analogous one of 2.135 Å in the  $\text{Ti}(\text{H}_2\text{O})^{1+}$  cluster at the SCF-MCPHF level [35]. In addition, the calculated O–H bond lengths  $R_2$  in the  $\text{Ti}(\text{H}_2\text{O})^{1+}$  clusters with spin numbers  $S = 1/2$  and  $3/2$  are 0.976 and 0.975 Å, respectively, values that also compare well with the O–H bond length of 0.966 Å in the  $\text{TiH}_3\text{OH}$  molecule at the CASSCF level [37]. The natural orbital population analysis charges and natural orbital electron configurations of the  $\text{Ti}(\text{H}_2\text{O})^{1+}$  clusters are listed in Table 6. In the most stable  $\text{Ti}(\text{H}_2\text{O})^{1+}$  cluster with  $S = 3/2$ , the natural orbital population analysis charge on the Ti atom is 0.937, whereas the natural orbital populations in its

3d and 4s subshells are 2.59 and 0.47, respectively. These two last values do not differ much from those of 2.24 and 0.84 obtained at the SCF-MCPHF level [35].

### 3.2. $\text{Ti}(\text{H}_2\text{O})_2^{0,\pm 1}$ clusters

Neutral  $\text{Ti}(\text{H}_2\text{O})_2^0$  clusters with  $C_1$  and  $D_{2d}$  point-group symmetries and with spin states  $S = 0, 1$  and  $2$  are optimized at the (U)B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis indicates that only the  $C_1$  clusters with spin numbers  $S = 0, 1$  and  $2$  are stable structures. However, those stable  $C_1$   $\text{Ti}(\text{H}_2\text{O})_2^0$  clusters are obtained by a slight distortion from the unstable  $D_{2d}$  structures. In the stable species, the Ti–O(1) and Ti–O(2) bond lengths  $R_1$  and  $R_2$  monotonically increase as the spin number  $S$  varies from 0 to 2, whereas the total energy  $E_T$  reaches a minimum with  $S = 1$ . Therefore, the  $\text{Ti}(\text{H}_2\text{O})_2^0$  cluster with  $S = 1$  is the most stable structure in the  $\text{Ti}(\text{H}_2\text{O})_2^0$  series of clusters. In that structure, both the Ti–O(1) and the Ti–O(2) bond lengths  $R_1$  and  $R_2$  are predicted to be 2.152 Å, values that are longer than the average Ti–O bond length of 1.79 Å at the CASSCF level [37]. In addition, the hydration dissociation energy  $DE_N(2, 1)$  in the  $\text{Ti}(\text{H}_2\text{O})_2^0$  cluster with  $S = 1$  is of

22.20 kcal/mol. The presently calculated values for bond lengths and hydration dissociation energy suggest once more that the interaction between the Ti and the O atoms in the  $\text{Ti}(\text{H}_2\text{O})_2^0$  clusters is of a weak van der Waals type. Finally, as can be seen from the data in Table 6, the Ti atoms remain almost uncharged upon coordination with the  $\text{H}_2\text{O}$  molecules in the  $\text{Ti}(\text{H}_2\text{O})_2^0$  clusters with  $S = 0, 1$  and  $2$ , as revealed by the Ti natural orbital population analysis charges of  $-0.0466, -0.0331$  and  $0.0582$ , respectively.

Cation  $\text{Ti}(\text{H}_2\text{O})_2^{1+}$  clusters with  $D_{2d}$  point-group symmetry and with spin numbers  $S = 1/2$  and  $3/2$  are optimized at the (U)B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis reveals that all the converged structures are stable. Present theoretical results listed in Table 2 show that the Ti–O(1) and Ti–O(2) bond lengths  $R_1$  and  $R_2$  slightly increase as the spin number  $S$  varies from  $1/2$  to  $3/2$ , whereas the most stable structure is that with spin number  $S = 3/2$ . The electronic state in that structure is  $^4A_2$ . In the most stable  $\text{Ti}(\text{H}_2\text{O})_2^{1+}$  cluster with  $S = 3/2$ , both the Ti–O(1) and the Ti–O(2) bond lengths  $R_1$  and  $R_2$  are predicted to be  $2.136 \text{ \AA}$  at the (U)B3LYP/LanL2DZ/6-31+G\* level, a value that successively is only slightly shorter than that of  $2.157 \text{ \AA}$  in the  $\text{Ti}(\text{H}_2\text{O})_2^{1+}$  cluster at the SCF-MCPF level [35], longer than the average Ti–O bond length of  $1.79 \text{ \AA}$  at the CASSCF level [37], and comparable with the Ti–O bond length predicted for the  $\text{Ti}(\text{H}_2\text{O})_6^{1+}$  cluster at the SCF-HF level [33]. The presently calculated hydration dissociation energy  $DE_C(2,1)$  for the most stable  $\text{Ti}(\text{H}_2\text{O})_2^{1+}$  cluster with  $S = 3/2$  is of  $30.1 \text{ kcal/mol}$ , a value that is  $5.1 \text{ kcal/mol}$  lower than the one predicted at the SCF-MCPF level [35]. Finally, in the same structure, the Ti atom natural orbital populations in its 3d and 4s subshells are  $2.65$  and  $0.51$ , respectively, values that do not differ much from their SCF-MCPF counterparts of  $2.43$  and  $0.73$ , respectively [35].

One anion  $\text{Ti}(\text{H}_2\text{O})_2^{1-}$  cluster with  $C_1$  point-group symmetry and with spin state  $S = 1/2$  is also optimized at the (U)B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis reveals this converged structure is stable. The calculated properties of this anion are listed in Tables 2 and 6.

### 3.3. $\text{Ti}(\text{H}_2\text{O})_3^{0,1+}$ clusters

Neutral and cation  $\text{Ti}(\text{H}_2\text{O})_3^{0,1+}$  clusters all with  $C_{3v}, C_{2v}$  and  $C_1$  point-group symmetries and with spin states  $S = 0, 1, 2$  for the neutral and  $S = 1/2, 3/2$  for the cation are optimized at the (U)B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis indicates that only the converged  $C_1$  structures are stable.

In the neutral  $\text{Ti}(\text{H}_2\text{O})_3^0$  clusters with spin numbers  $S = 0, 1$  and  $2$ , the Ti–O(2) and Ti–O(3) bond lengths  $R_2$  and  $R_3$  and also the O(1)–Ti–O(2) bond angle  $\alpha_1$  monotonically decrease as the spin number  $S$  varies from  $0$  to  $2$ , whereas the total energy  $E_T$  reaches a minimum with

$S = 1$ . Therefore, the  $\text{Ti}(\text{H}_2\text{O})_3^0$  cluster with spin number  $S = 1$  is the most stable structure in this  $\text{Ti}(\text{H}_2\text{O})_3^0$  series of clusters. In that structure, the Ti–O bond lengths exhibit relatively elongated values of about  $2.1\text{--}2.3 \text{ \AA}$ , whereas its predicted hydration dissociation energy  $DE_N(3,2)$  is of  $7.51 \text{ kcal/mol}$ . Once again, all those calculated values seem to be consistent with weak van der Waals interactions between the Ti and the O atoms. In the most stable  $\text{Ti}(\text{H}_2\text{O})_3^0$  cluster with spin  $S = 1$ , the natural orbital populations in the 3d and 4s subshells of the Ti atom are  $2.50$  and  $1.45$ , respectively, whereas that atom natural orbital population analysis charge is  $0.0175$ .

In the cationic  $\text{Ti}(\text{H}_2\text{O})_3^{1+}$  clusters with spin numbers  $S = 1/2$  and  $3/2$ , the three Ti–O(1), Ti–O(2) and Ti–O(3) bond lengths  $R_1\text{--}R_3$  monotonically increase as the spin number varies from  $1/2$  to  $3/2$ , whereas the total energy  $E_T$  reaches a minimum with  $S = 3/2$ . Therefore, the  $\text{Ti}(\text{H}_2\text{O})_3^{1+}$  cluster with  $S = 3/2$  is the most stable structure in the  $\text{Ti}(\text{H}_2\text{O})_3^{1+}$  series of clusters. The electronic state in that structure is  $^4A$ . In the  $\text{Ti}(\text{H}_2\text{O})_3^{1+}$  cluster with  $S = 3/2$ , the presently calculated Ti–O(2) bond length  $R_2$  of  $2.151 \text{ \AA}$  agrees well with that of  $2.157 \text{ \AA}$  in the related  $\text{Ti}(\text{H}_2\text{O})_2^{1+}$  at the SCF-MCPF level [35]. The predicted hydration dissociation energy  $DE_N(3,2)$  in the most stable  $\text{Ti}(\text{H}_2\text{O})_3^{1+}$  cluster with  $S = 3/2$  is  $30.16 \text{ kcal/mol}$  at the (U)B3LYP/LanL2DZ/6-31+G\* level, a value that is bigger than that reported by Armentrout et al. [28]. Finally, the presently calculated natural orbital populations in the 3d and 4s subshells of the Ti atom in the most stable  $\text{Ti}(\text{H}_2\text{O})_3^{1+}$  cluster with  $S = 3/2$  are  $2.65$  and  $0.54$ , respectively, whereas that atom natural orbital population analysis charge is of  $0.7988$ .

### 3.4. $\text{Ti}(\text{H}_2\text{O})_4^{0,1+}$ clusters

Neutral  $\text{Ti}(\text{H}_2\text{O})_4^0$  clusters with  $C_1$  point-group symmetry and with spin states  $S = 0, 1$  and  $2$  are optimized at the (U)B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis reveals that all these converged structures are stable. Inspection of the total energies  $E_T$  listed in Table 4 reveals that the almost planar  $\text{Ti}(\text{H}_2\text{O})_4^0$  cluster with spin number  $S = 1$  is the most stable structure in this series of  $\text{Ti}(\text{H}_2\text{O})_4^0$  clusters. In that structure, the predicted Ti–O bond lengths  $R_1\text{--}R_4$  are all nearly  $2.1\text{--}2.2 \text{ \AA}$ , whereas the O–H bond lengths are around  $0.98 \text{ \AA}$ . In the most stable  $\text{Ti}(\text{H}_2\text{O})_4^0$  cluster with  $S = 1$ , the presently calculated Ti–O(1) and Ti–O(2) bond lengths  $R_1$  and  $R_2$  of  $2.172$  and  $2.179 \text{ \AA}$ , respectively, and also the H–O–H bond angles are comparable to theirs analogous ones of  $2.180 \text{ \AA}$  and  $108.2^\circ$  in the related  $\text{TiH}_3\text{OH}$  molecule at the CASSCF level [37]. In addition, the predicted hydration dissociation energy  $DE_N(4,3)$  for the most stable  $\text{Ti}(\text{H}_2\text{O})_4^0$  cluster with  $S = 1$  is of  $4.82 \text{ kcal/mol}$ .

Cation  $\text{Ti}(\text{H}_2\text{O})_4^{1+}$  clusters with  $C_1$  point-group symmetry and with spin states  $S = 1/2$  and  $3/2$  are optimized at the (U)B3LYP/LanL2DZ/6-31+G\* level. Subsequent harmonic vibrational frequency analysis reveals that all the

converged structures are stable. Inspection of the calculated total energies  $E_T$  in Table 4 reveals that the  $\text{Ti}(\text{H}_2\text{O})_4^{1+}$  cluster with spin number  $S = 3/2$  is the most stable structure in this  $\text{Ti}(\text{H}_2\text{O})_4^{1+}$  series of clusters. In that structure, the presently calculated hydration dissociation energy  $DE_C(4,3)$  is of 20.18 kcal/mol, a value that is in good agreement with that of 19.9 kcal/mol reported by Armentrout et al. [28]. Finally, inspection of the calculated natural orbital population analysis charges in Table 6 indicates that the charges on the Ti atoms of the  $\text{Ti}(\text{H}_2\text{O})_4^{1+}$  clusters monotonically decrease as the spin number  $S$  varies from  $1/2$  to  $3/2$ . This charge decrease should be attributed to increasing electron transfers from the coordinated  $\text{H}_2\text{O}$  molecules to the central  $\text{Ti}^{1+}$  ion.

### 3.5. $\text{Ti}(\text{H}_2\text{O})_5^{0,1+}$ clusters

Neutral and cation  $\text{Ti}(\text{H}_2\text{O})_5^{0,1+}$  clusters with  $C_1$  symmetry and with spin states  $S = 0, 1, 2$  for the neutral, and  $S = 1/2, 3/2$  for the cation are optimized at the (U)B3LYP/LanL2DZ/6-31+G\* level. The geometry initial guesses for all these  $\text{Ti}(\text{H}_2\text{O})_5^{0,1+}$  species are generated from its nearly planar  $\text{Ti}(\text{H}_2\text{O})_4^{0,1+}$  relatives with a fifth  $\text{H}_2\text{O}$  molecule capped on top. Subsequent harmonic vibrational frequency analysis reveals that all the converged structures are stable. In the neutral  $\text{Ti}(\text{H}_2\text{O})_5$  clusters, inspection of their total energies  $E_T$  in Table 5 reveals that the cluster with spin number  $S = 1$  is the most stable structure in this series. In that structure, the predicted hydration dissociation energy  $DE_N(5,4)$  is of 10.11 kcal/mol. Meanwhile, in the cationic  $\text{Ti}(\text{H}_2\text{O})_5^{1+}$  clusters, inspection of their total energies  $E_T$  in Table 5 shows that the cluster with spin number  $S = 3/2$  is the most stable structure in this series, although this cation is only slightly lower in energy than its counterpart with  $S = 1/2$ . In the most stable  $\text{Ti}(\text{H}_2\text{O})_5^{1+}$  with  $S = 3/2$ , the presently predicted hydration dissociation energy  $DE_C(5,4)$  is of 13.78 kcal/mol. Finally, the calculated natural orbital populations and natural orbital population analysis charges in the  $\text{Ti}(\text{H}_2\text{O})_5^{0,1+}$  clusters can be examined in Table 6.

## 4. Concluding remarks

The full series of the  $\text{Ti}(\text{H}_2\text{O})_n^{0,1+}$  ( $n = 1-5$ ) clusters have been herein systematically investigated at the (U)B3LYP/LanL2DZ/6-31+G\* level of theory for the first time. Several molecular properties have been calculated for the clusters stable structures, including optimal geometries, total energies, bond lengths, bond angles, natural orbital population analysis charges, and hydration dissociation energies inter alia. Due to the weak interactions between the Ti ( $\text{Ti}^{1+}$ ) atom (ion) and the  $\text{H}_2\text{O}$  molecules, specially in the case of the neutral clusters, convergence by the self-consistent field algorithm of the (U)B3LYP/LanL2DZ/6-31+G\* method was difficult to reach. In addition, some converged structures were proven to be unstable under subsequent harmonic vibrational frequency analysis. The present re-

sults show a strong correlation between the clusters total energy  $E_T$  and their spin states. Without exception, the most stable neutral cluster  $\text{Ti}(\text{H}_2\text{O})_n^{0+}$  ( $n = 1-5$ ) in each series of hydrates with  $n\text{H}_2\text{O}$  molecules is that with spin state  $S = 1$  (triplet state), and the most stable cationic cluster  $\text{Ti}(\text{H}_2\text{O})_n^{1+}$  ( $n = 1-5$ ) in each series of hydrates with  $n\text{H}_2\text{O}$  molecules is that with spin state  $S = 3/2$  (quadruplet state). For all the structures, the Ti–O bond lengths are always in the range of about 2.0–2.5 Å, values that are longer than the average Ti–O bond length. In many neutral clusters, natural orbital population analysis charges on the Ti atom are negligible thereby indicating no appreciable electron transfers with the coordinated  $\text{H}_2\text{O}$  molecules. Relevant hydration dissociation energies have been reported and discussed as well. The calculated properties are consistent with relatively weak interactions between the Ti ( $\text{Ti}^{1+}$ ) atom (ion) and the  $\text{H}_2\text{O}$  molecules, predominantly of the van der Waals and of the charge-permanent dipole types in the neutral and the cationic clusters, respectively. In the specific case of the neutral species, chemical intuition and the obtained long bond distances, low hydration dissociation energies and negligible atomic charges suggest Ti– $\text{H}_2\text{O}$  van der Waals interactions. However, caution must be exerted on that conclusion because it is not yet possible to describe correctly van der Waals (dispersive) interactions with DFT using the local density approximation, the generalized gradient approximation, or hybrid exchange-correlation functionals. Moreover, some exchange-correlation potentials can show spurious binding in van der Waals complexes [47,48] although new DFT functionals have been proposed to correctly describe dispersive interactions [49–54]. Comparison of some calculated properties at the (U)B3LYP/LanL2DZ/6-31+G\* level with a few available results for aqueous titanium clusters and for related titanium-bearing molecules shows good agreement. Present research efforts are directed to a further theoretical characterization of aqueous titanium-bearing clusters and also of related aqueous clusters containing other transition metals (e.g., Cr [55]).

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